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A Bis(germaamidine) through Nitrene Insertion into Ge—Si Bonds

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Dedicated to Professors Franc Meyer and Christian Limberg on the occasion of their combined 120th birthday

Amidines (with two nitrogen atoms around the unsaturated carbon center) are important synthetic building blocks. In particular, phenylene-bridged derivatives are extensively used in the synthesis of cyclic and polymeric structures for pharmaceutical, electrochemical, and materials applications. While various heavier Group 14 congeners of the related imines and guanidines (with one nitrogen less or more, respectively) are known, only one case of an amidine with a Sn═N bond has been reported. Herein, a bis(germaamidine) with the two germaamidine moieties connected by a silylene-phenylene linking unit is presented. Azide-induced Ge═Ge double bond cleavage in the bridged bis(digermene) precursor results in the concomitant formation of two equivalents of a tetraazagermole by-product. NMR spectroscopic monitoring and the isolation of an intermediately occurring aziridine suggest the initial formation of a bis(germaimine), followed by the insertion of transient nitrene into the Ge—Si bonds. This is further confirmed by comparative reactions of the Ge(II) centers of the corresponding bis(germylene)-carbene adducts with the azide. Reactions of the bis(germaamidine) with CO_2 and MeOH result in additions to the Ge═N bonds, suggesting significant potential as a bifunctional monomer for the synthesis of poly(germane)s.

1. Introduction

Amidines with their amino-functionalized C═N double bonds constitute important synthons in organic chemistry.[1] In particular, phenylene-bridged dimers are used for the construction of cyclic, oligomeric, and polymeric structures for pharmaceutical purposes and applications in the electrochemical CO_2 conversion, fast-charging lithium-ion batteries, or as phase-change materials for energy storage.[2] During the past decades, extensive research on the heavier Group 14 element analogs of multiply bonded compounds has provided insights into their structure-function relationship and has resulted in the development of new materials and catalytic syntheses.[3] Nonetheless, stable congeners with element-nitrogen double bonds are still rare, particularly bridged derivatives: for instance, there is only one report on bifunctional germaimines, bridged between the imino functions.[4]

The tendency of the polar the E^{14}═N bond to dimerize via cycloaddition constitutes a challenge for the isolation of base-free heavier imine analogues. While in the case of silicon, cyclic and acyclic homoleptic dialkyl substituted representatives have been stabilized through the use of sterically demanding substituents,[5] related silaguanidines and silaamidines require additional intra- or intermolecular base stabilization (**A**, **Scheme 1**).[6] For the heavier elements germanium and tin, bulkier substituents enabled the isolation of stable donor-free analogs,[4,7] and the use of π-donor substituents has resulted in a number of heavier guanidine derivatives (**B**).[8] The use of a sterically demanding terphenyl substituent has just recently provided a stannaamidine—an unprecedented example of a heavier Group 14 amidine (**C**).[9] Accordingly, the isolation of a germaimidoyl chloride has been accomplished with an extremely bulky hydrindacene ligand;[7c] however, germaamidines with only one amino substituent adjacent to the Ge═N bond still remain unknown as of today.

Germaimines **I** and germaguanidines **II** with various different substituents are, without exception, obtained via reactions of the corresponding germylenes with azides as a source of nitrenes.[4,7,8c-g] An intramolecularly stabilized cyclic analogue by Veith et al.[10] and donor-free oxygen- and ferrocene-bridged compounds have been synthesized accordingly.[8e,g] In contrast, the reaction of a (silyl)(amidinato)germylene with 1-adamantylazide has recently been reported to result in the insertion of a nitrene into the Ge—Si bond instead.[11] Digermenes, on the other hand, have been shown to form digermaaziridines **III** in reactions with azides, presumably via N_2 elimination from the intermediately occurring 1,2-digerma-3,4,5-triazoles (**Scheme 2**).[12]

We recently reported on σ,π-conjugated polymers with *para*-silylenephenylene bridged Ge═Ge double bonds obtained from the bis(digermene) monomers in the heavier acyclic diene metathesis.[3r,s] In order to further elaborate the structure-function relationship of these materials with regard to the design of

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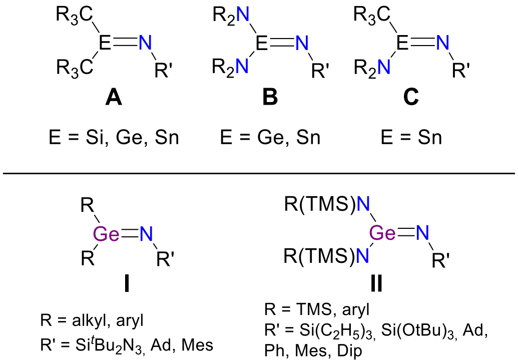


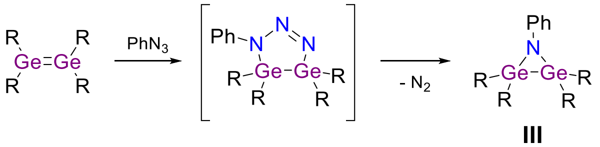
Scheme 1. Top: Heavier Group 14 systems with element-nitrogen double bonds: heavier imines **A**, guanidines **B**, and amidines **C**. Bottom: Reported acyclic germaimines **I** and germaguanidines **II** (Ad = 1-adamantyl, Mes = 2,4,6-trimethylphenyl, TMS = trimethyl silyl, Dip = 2,6-diisopropylphenyl).

new materials with variable properties, the reactivities of the bis(digermene) monomers and the intermediate low-valent bis(germylene)s[13] are of particular interest.

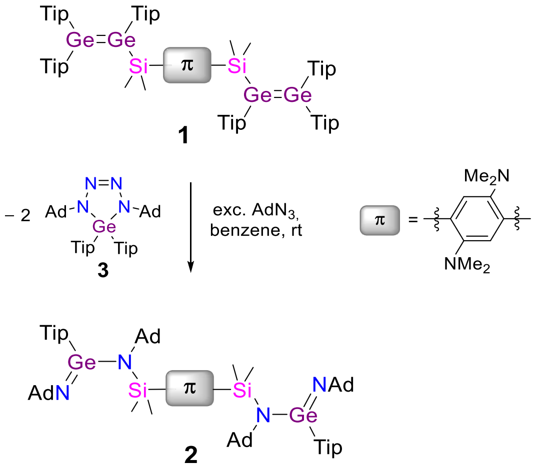
Herein, we report the reactions of a bis(digermene) and an N-heterocyclic carbene (NHC)-bis(germylene) with 1-adamantyl azide, resulting in the formation of a bis(germaamidine) with a *para*-silylene-phenylene linking unit between the two low-coordinate germanium centers. Furthermore, the reactivity of the resulting Ge=N bonded species toward carbon dioxide and methanol was probed.

2. Results and Discussion

The addition of an excess of 1-adamantyl azide to a yellow solution of bis(digermene) **1** (**Scheme 3**) in benzene at room temperature results in the immediate liberation of a gas, indicating the release of N_2. NMR spectroscopy confirms quantitative conversion of the starting material. The presence of only one peak in the ^{29}Si NMR spectrum at −5.4 ppm suggests the formation of a single symmetrical product containing the silylene-phenylene linker. Regarding the reported reactivity of digermenes toward azides (vide supra), we expected cycloaddition reactions between the Ge=Ge double bonds and the azide or the derived nitrene, i.e., the formation of either 1,2-digerma-4,5,6-triazoles, digermaaziridines, or 1,3-digerma-2,4-diazetidines. Unexpectedly, however, single crystal X-ray analysis of colorless crystals obtained from a concentrated benzene solution in 69% yield revealed the constitution of **2** (**Figure 1**, top). The bis(germaamidine) **2** is stable in the solid state and in solution at room temperature in the absence of air and moisture, but decomposes unselectively at its melting point of 202 °C. From the mother liquor, tetraazagermole **3** crystallized in 60% yield and was thus confirmed as major by-product of the reaction, explaining the fate of the $GeTip_2$ moiety (Figure 1, bottom).



Scheme 2. Reactions of digermenes with phenylazide result in digermaaziridines **III** (R = 2,6-diethylphenyl or 2,4,6-trimethylphenyl).



Scheme 3. Reaction of bis(digermene) **1** with an excess of 1-adamantyl azide to bis(germaamidine) **2** and tetraazagermole **3** (Ad = 1-adamantyl, Tip = 2,4,6-triisopropylphenyl).

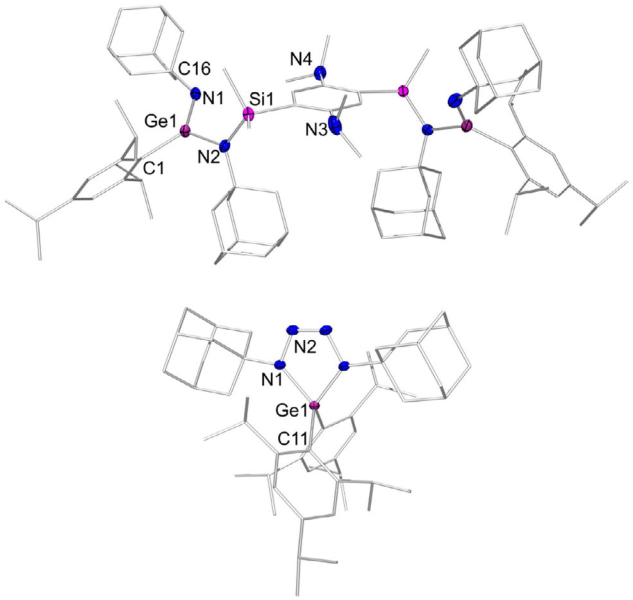


Figure 1. Molecular structures of bis(germaamidine) **2** (top) and tetraazagermole **3** (bottom) in the solid state (co-crystallized solvent molecules, hydrogen atoms, and disordered atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1—N1 1.695(4), Ge1—N2 1.837(4), Si1—N2 1.747(4), Si1—N1 3.608(3), Σ°(Ge1) 360.0(6), Σ°(N2) 360.0(8), N1-Ge1-N2-Si1 51.5(2) (**2**); Ge—N1 1.894(2), N1—N2 1.383(3), N2—N2 1.256(4), C11-Ge-C11′ 105.6(1), Σ° 539.9(5), N1-Ge-N1′-C11-Ge-C11′ 16.34(6) (**3**).

The molecular structure of bis(germaamidine) **2** in the solid state exhibits two different germanium–nitrogen bond distances, suggesting distinct double and single bond character, respectively

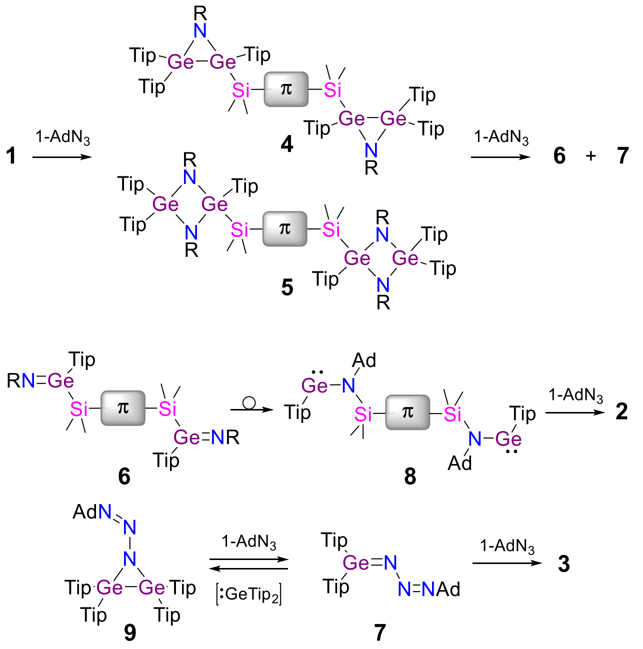
(Ge1—N1 1.695(4), Ge1—N2 1.837(4) Å). Both bonds are at the shorter end of reported Ge—N distances in guanidine analogs with two amino groups adjacent to the double bond (Ge=N: 1.69–1.72 Å, Ge–N: 1.80–1.90 Å).[8c–g] The Ge1 center and the singly bonded N2 both show planar coordination (Σ°(Ge1) 360.0(6)°, Σ°(N2) 360.0(8)°), likewise similar to the germaguanidines, with a dihedral angle of 51.5(2)° between the bonding planes. The *syn* conformation exhibited in the crystal structure is expected to be sterically and electronically favored due to potentially weak donor–acceptor interactions between the imine nitrogen and the silane (Si1—N1 3.608(3) Å). Notably, the adamantyl substituents at both amines are at the same site of the phenylene plane, despite the steric demand and hence likely due to favorable dispersion interactions.

In line with nitrogen substitution at silicon (silylamines: −5 to −1 ppm),[14] the ^{29}Si NMR resonance (−5.4 ppm) is upfield-shifted compared to bis(digermene) **1** (4.3 ppm).[3r] Our recently reported amide-functionalized NHC-bis(germylene) with the same silylene-phenylene linker yet without Ge=N double bonds exhibits similar shifts (−6.3, −6.4 ppm),[15] indicating comparable delocalization of the nitrogen lone-pair in line with the planar arrangement at the amine nitrogen atoms.

The N1—N2 bonds (1.383(3) Å) in tetraazagermole **3** (Figure 1) are slightly shortened compared to typical planar N—N single bonds (≈1.401 Å),[16] and the N2—N2 bond (1.256(4) Å) is accordingly elongated (*cis*-substituted N=N double bonds: ≈1.245 Å).[16] This effect is less pronounced than in known tetraazagermoles, which all exhibit π-donor substituents at the germanium center (N—N: 1.36–1.41 Å, N=N: 1.26–1.27 Å, Ge—N 1.83–1.85 Å).[7c,17] The Ge—N1 single bonds in **3** (1.894(2) Å) are significantly elongated in comparison with **2** (1.837(4) Å), presumably due to the distinct steric demand of the Tip and adamantyl groups in **3**. The five-membered ring is planar (sum of the inner angles Σ° 539.9(5)°), as in reported structures (538 to 540°).

The net reaction of bis(digermene) **1** with 1-adamantyl azide formally cleaves the Ge=Ge double bonds homolytically. For the formation of bis(germaamidine) **2**, two equivalents of 1-adamantyl nitrene (provided by the azide under N_2 elimination) form the Ge=N double bonds and two further equivalents insert into the Ge—Si bonds. In light of the fact that homolytic Ge=Ge bond cleavage in **1** only occurs at 65 °C in the absence of an initiator, according to our reports on the reactions toward trialkylsilane and carbenes as well as its polymerization at 65 °C,[3r,13] we tentatively propose the initial formation of transient aziridine **4** and possibly also azetidine **5** derived from silylene-phenylene bridged bis(digermene) **1** (**Scheme 4**). These highly strained cyclic structures are expected to readily release transient bis(germaimine) **6** as well as Tip$_2$Ge=N$_3$Ad **7**. Indeed, ^{1}H NMR analysis of a reaction mixture of bis(digermene) **1** and eight equivalents of 1-AdN$_3$ shows the formation of bis(germaamidine) **2** in a 1:2 ratio with peaks in line with Tip$_2$Ge=N$_3$Ad, which subsequently decreases in favor of tetraazagermole **3**.

The transient formation of bis(germaimine) **6** is further supported by the mechanistic studies by Sen et al., which suggested a mono(germaimine) similar to **6** as a key intermediate in the net insertion reaction of a nitrene into the Ge—Si bonds of a silyl mono(germylene).[11] In line with this, we postulate the formation of bis(aminogermylene) **8** via the corresponding rearrangement of bis(germaimine) **6** (Scheme 4). The reaction of **8** with two additional equivalents of nitrene generated from 1-AdN$_3$ should then provide the final bis(germaamidine) **2**. Notably, in a reaction of bis(digermene) **1** with hexanol, the Ge—Si bonds are cleaved as well, yielding an alkoxylated bis(silane) while the Ge=Ge moiety undergoes unselective decomposition (for details see Supporting Information).



Scheme 4. Proposed intermediates aziridine **4** and azetidine **5** for the formation of transient germaimines **6** and **7** (top), subsequent formation of bis(germaamidine) **2** via bis(aminogermylene) **8**, and proposed reactions of **7** with 1-adamantyl azide to tetraazagermole **3** and with Tip$_2$Ge to digermaaziridine **4** (Ad = 1-adamantyl, Tip = 2,4,6-triisopropylphenyl, R = N$_2$Ad).

Unfortunately, all attempts to isolate key intermediates containing the silylene-phenylene backbone by applying variable azide deficiencies at low temperatures resulted in unidentified reaction mixtures. Nonetheless, the reaction of **1** with two equivalents of 1-AdN$_3$ at −85 °C yielded a few crystals of the three-membered ring **9** (**Figure 2**). The formation of **9** can be rationalized by a [2 + 2]-cycloaddition of intermediate Tip$_2$Ge=N$_3$Ad and diarylgermylene Tip$_2$Ge due to an insufficient amount of the azide present in the reaction mixture (Scheme 4).

The structure of **9** is similar to Weidenbruch's digermaaziridines obtained from the reaction of Tip$_2$Ge=GeTip$_2$ with diazomethanes:[18] the Ge1—Ge2 bond length (2.4368(3) Å) indicates a single bond, in line with a genuine cyclopropane structure and no π-interaction. Tip$_2$Ge=GeTip$_2$ is typically formed immediately upon Tip$_2$Ge release in the absence of a suitable trapping reagent.[3r,13] In contrast to the reported reactivity toward diazomethanes, however, we did not observe the conversion of Tip$_2$Ge=GeTip$_2$ to **9** in the presence of 1-AdN$_3$, even at 65 °C. This is attributed to the higher steric demand of the adamantyl substituent in comparison to the CH$_2$ and CHSiMe$_3$ groups in the

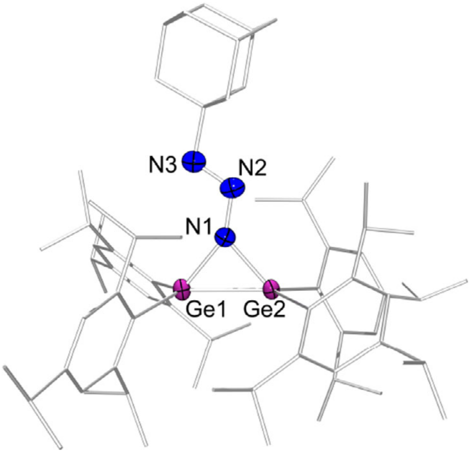
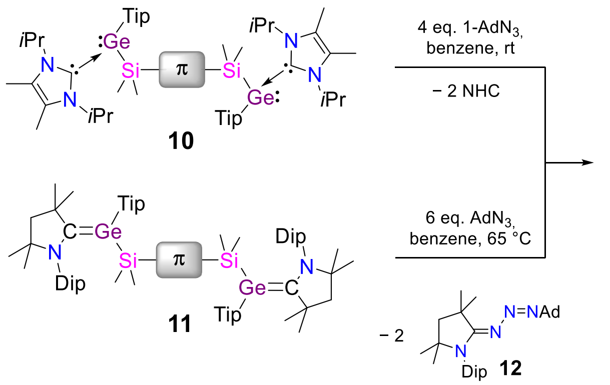


Figure 2. Molecular structures of digermaaziridine **9** in the solid state (hydrogen atoms and disordered atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.4368(3), Ge2–N1 1.8766(18), Ge2–N1 1.9088(18), N1–N2A 1.360(4), N2A–N3A 1.249(4), Ge1-N1-Ge2 80.13(7), N1-Ge1-Ge2 49.35(5), N1-Ge2-Ge1 50.51(5).

reported digermaaziridines[18] and supports the formation of **9** via the proposed [1 + 2] cycloaddition of $\text{Tip}_2\text{Ge{=}N}_3\text{Ad}$ with Tip_2Ge.

Only recently, we reported the trapping of a transient bis(silylgermylene) as its adducts with an NHC and a cyclic (alkyl)(amino) carbene (CAAC), **10** and **11** (**Scheme 5**).[13] The selective insertion of mildly electrophilic heteroallenes (CO_2 and ^{Et}NCO) into the Ge—Si bonds of **10** occurred under retention of the Ge(II) centers, presumably due to the NHC donor stabilization.[15] The related reactivity of a silylgermylene toward 1-adamantyl azide, reported by Sen et al., resulted in the insertion of nitrenes into the Ge—Si bond and retention of the Ge(II) center, intramolecularly stabilized by an amidinato substituent.[11]

These results spurred our interest in the reactivity of NHC-bis(germylene) **10** toward azides. The addition of 1-adamantyl azide to **10** in benzene provoked immediate gas formation, indicating the release of N_2, concomitant with consecutive color changes from yellow to red and finally pale yellow. Surprisingly, NMR spectroscopy confirmed the formation of bis(germaamidine) **2** and free NHC[19] (Scheme 5). In line with that, four equivalents of the azide were required to achieve full conversion of bis(germylene) **10**. Bis(germaamidine) **2** was obtained in 39% yield after washing the colorless solid with pentane.



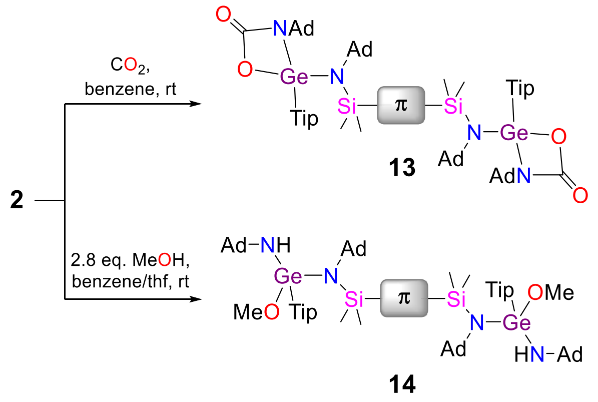
Scheme 5. Formation of bis(germaamidine) **2** from NHC- and CAAC-stabilized bis(germylene)s **10** and **11** and concomitant formation of by-product **12** (NHC = 1,3-diisopropylimidazol-4,5-dimethyl-2-ylidene, Tip = 2,4,6-triisopropylphenyl, Ad = 1-adamantyl).

In order to shed further light on the mechanism, we measured variable temperature ^{1}H NMR spectra at low temperatures, which showed complete conversion of **10** at −80 °C. Only when heating to −10 °C, however, the formation of bis(germaamidine) **2** and free NHC was observed. Consequently, NHC-coordinated bis(aminogermylene) **8** might reasonably form as an intermediate prior to the addition of two additional nitrenes to both germanium lone pairs at −10 °C and the resulting release of the NHC. Unfortunately, the complexity of the NMR spectra at −80 °C indicated a mixture of several intermediates in line with the only moderate yield of **2** under these conditions.

Notably, the reaction of CAAC-bis(germylene) **11**, in stark contrast to digermene **1** and NHC-germylene **10**, did not proceed at all at ambient temperature, most likely due to the considerably stronger interaction of the germanium(II) centers with the carbenes.[13,15] After heating a mixture of **11** and 1-AdN$_3$ at 65 °C overnight, bis(germaamidine) **2** was obtained in 68% yield after workup (Scheme 5). Six equivalents of the azide were necessary to achieve complete conversion of **11**, in line with the formation of two equivalents of CAAC–N$_3$Ad **12** as the by-product. For confirmation, we independently synthesized CAAC–N$_3$Ad **12** (C_{CAAC}–N 1.307(2) Å, δ^{13}C 178.0 ppm) by straightforward reaction of the CAAC with 1-adamantyl azide in a 1:1 ratio, in analogy to the recently reported CAAC-adducts of terphenyl azides with similar structural features and NMR data (C_{CAAC}–N 1.32 and 1.39 Å, δ^{13}C 179.0 and 180.8 ppm).[20]

Similar to silylene-phenylene bridged bis(digermene) **1**[3s] and to both carbene-adducts of the corresponding bis(germylene) **10** and **11**,[13] density functional theory calculations on **2** indicate the presence of σ,π-conjugation between the germaamidine moieties: the in-phase and out-of-phase combinations of the π-orbitals on both sides of the linking unit are separated by as much as 0.08 eV due to mutual interaction. Furthermore, the lowest unoccupied π^*-orbital located at the phenylene moiety is the LUMO + 4 and thus relatively high in energy (for details see Supporting Information). This is in notable contrast to the acyl bis(germylene)s recently reported by us with carboxy or amide groups that clearly interrupt the interaction between the Ge(II) end groups.[15]

In light of the rising interest in polymers with heavier p-block elements[21] and inspired by the reactivity of a germaguanidine toward C=O bonds reported by Fulton et al.,[8f] we became interested in [2 + 2]-cycloaddition reactions at the Ge=N double bonds. Hence, we exposed bis(germaamidine) **2** to carbon dioxide. The Ge=N bonds in **2** proved indeed suitable for CO_2 activation, providing the corresponding cycloaddition product bis(germaoxazetidinone) **13** (**Scheme 6**). The crude reaction mixture contains a diastereomeric mixture of the racemate and the *meso*-form, according to the presence of two sets of signals in the heteronuclear NMR spectra. The *meso*-form is obtained in pure



Scheme 6. Reaction of bis(germaamidine) **2** with CO_2 and MeOH to bis(germaoxazetidinone) **13** and hydroalkoxylation products **14** (Tip = 2,4,6-triisopropylphenyl, Ad = 1-adamantyl).

form upon crystallization from benzene in 40% yield (**Figure 3**, top). The C═O bonds give rise to a characteristic band at 1720 cm^{-1} in the IR spectrum and a ^{13}C NMR resonance at low field (157.6 ppm), comparable to the corresponding carbamate obtained from the monomeric guanidine derivative reported by Fulton et al. (159.7 ppm).[8f] The ^{29}Si NMR peak (−5.2 ppm) of **13** is almost identical to that of the bis(germaamidine) starting material **2** (−5.4 ppm).

The single crystal X-ray structure of **13** (Figure 3, top) reveals almost perfectly planar oxazetidine rings with a sum of the inner angles of 359.9(1)°. Coordination at the amine nitrogen atoms, in particular at the exocyclic ones, deviates from planarity with sums of the angles of Σ°(N1) 357.1(4)° and Σ°(N2) 355.7(3)°, in contrast to amidine **2**, which exhibits considerable delocalization of the nitrogen lone-pairs across the Ge═N bonds. Notably, the endocyclic Ge1–N1 (1.878(2) Å) bonds are slightly elongated in

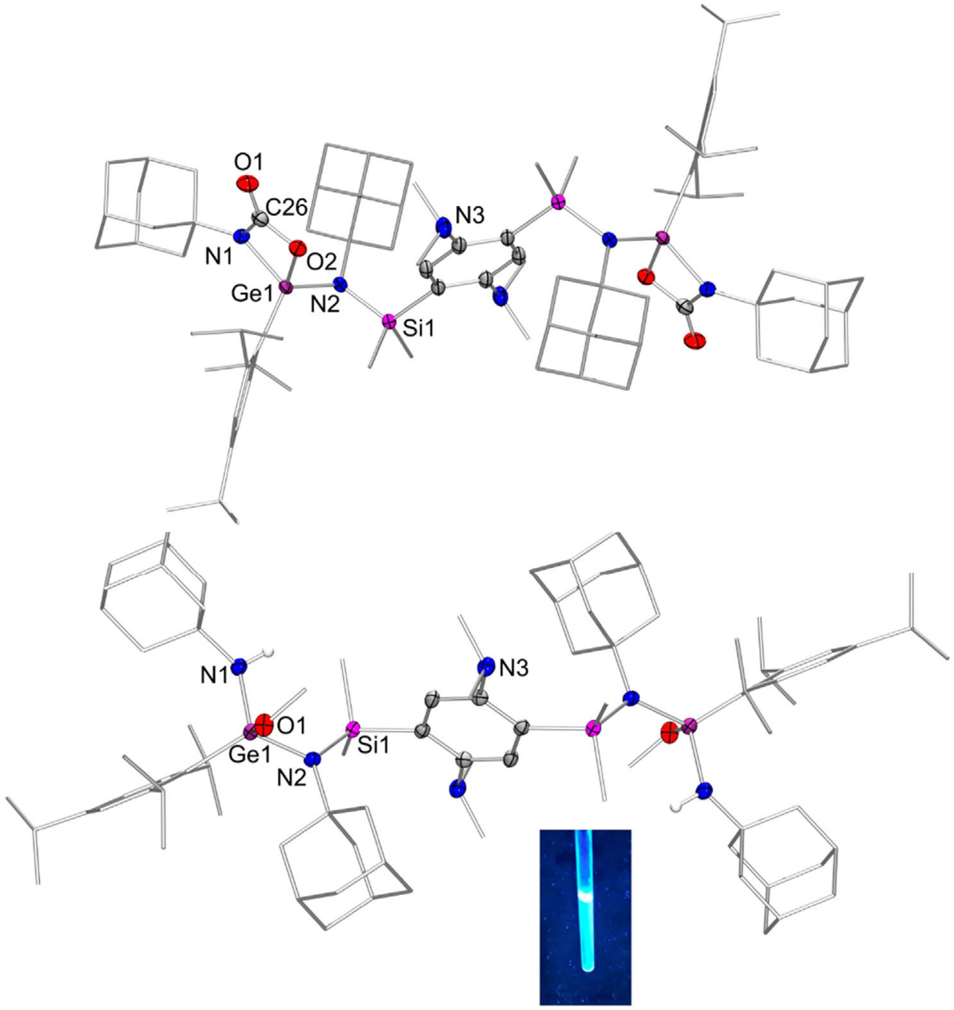


Figure 3. Molecular structures of bis(germaoxazetidinone) **13** (top) and the hydroalkoxylation product **14** (bottom) in the solid state (co-crystallized solvent molecules, hydrogen atoms, and disordered atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1–N1 1.878(2), Ge1–N2 1.838(2), Ge1–O2 1.867(1), Σ° 359.9(1), Σ°(N1) 357.1(4), Σ°(N2) 355.7(3). (**13**) Ge1–O1 1.810(2), Ge1–N1 1.829(3), Ge1–N2 1.874(2), Si1-N2-Ge1 126.5(1), C26-N2-Ge1 115.4(2), C26-N2-Si1 118.0(2), Σ°(N2) 359.9(5) (**14**). Inset: Image of intense blue fluorescence of **14** under UV irradiation (λ_{exc} = 254 nm).

comparison to the Ge1-N2 bonds (1.838(2) Å), in line with Fulton's observations (1.876 vs. 1.805 and 1.804 Å).[8f]

A corresponding acyclic structure was obtained by the twofold addition of methanol to bis(germaamidine) **2** (Scheme 6) to yield **14** with similar NMR data as **13**, but exhibiting additional resonances in the ^{1}H NMR spectrum at 1.60 ppm (1H, NH) and at 3.51 ppm (3H, MeO). Single crystals of **14** suitable for X-ray analysis were obtained from a benzene solution (Figure 3, bottom). The decreased structural constraint in comparison to bis(germaoxazetidinone) **13** results in the planarization of the amine ($\Sigma°$(N2) 359.9(5)°). The ^{29}Si NMR peaks of the obtained diastereomeric mixture (−7.05, −7.09 ppm) are marginally upfield shifted compared to **13** (−5.18 ppm) and bis(germaamidine) **2** (−5.40 ppm). Notably, **14** exhibits intense blue fluorescence ($\lambda_{em} = 436$ nm) under UV light irradiation (Figure 3, inset). A huge Stokes shift of $\Delta\lambda = 223$ nm with regard to the longest wavelength absorption maximum at $\lambda_{abs} = 213$ nm is observed, suggesting considerable relaxation of the vertically excited state.[22] The luminescence of **14**—in contrast to all other species described herein—suggests a shutdown of non-radiative decay of the excited state.

3. Conclusion

We have reported a bis(germaamidine), i.e., a species containing two Ge═N motifs with just one additional Ge─N single bond at each Ge center that are connected by a silylene-phenylene linker. In contrast to reported mono(germaguanidines), which are formed in reactions of amino germylenes with azides, the bis(germaamidine) was obtained from the corresponding silyl bis(digermene). A sterically encumbered tetraazagermole is formed as a systematic by-product of the reaction, scavenging the liberated GeTip$_2$ germylenes. According to NMR spectroscopic investigations and the corresponding reactions of the NHC- and CAAC-stabilized bis(germylene)s, azide-induced Ge═Ge double bond cleavage is followed by nitrene migrational insertion into the Ge─Si bonds and subsequent addition of another equivalent of nitrene to the Ge(II) centers. The bis(germaamidine) readily reacts with CO$_2$ and methanol in addition reactions, showcasing great potential for the application in the synthesis of bridged poly(germane)s and their postfunctionalization. The intense fluorescence with a huge Stokes shift of the methanol addition product suggests a possible application in optoelectronics.

4. Experimental Section

General Remarks: All manipulations were carried out under a protective atmosphere of argon, applying standard Schlenk or glovebox techniques. The glassware was predried in an oven at 125 °C and heated in vacuo prior to use. Solvents were taken from a solvent purification system (Innovative Technology PureSolv MD7 or MBraun SPS 5/7; diethyl ether, hexane, pentane, THF, benzene, toluene). Benzene-d$_6$ and THF-d$_8$ were dried over a potassium mirror, degassed through freeze-pump-thaw cycles, and condensed under argon prior to use. Bis(digermene) **1**,[3r] NHC-bis(germylene) **10**,[13] CAAC-bis(germene) **11**,[13] 1,3-bis(2,6-diisopropyl)imidazol-2-ylidene (NHC),[19] 1-(2,6-diisopropylphenyl)−3,3,5,5-tetramethyl-pyrrolidin-2-ylidene (CAAC),[23] were prepared according to published procedures. All other chemicals were obtained commercially and used as received. The NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer at 300 K (^{1}H: 400.13 MHz, ^{13}C: 100.6 MHz, ^{29}Si: 79.5). The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton and natural abundance ^{13}C resonances of the deuterated solvent and chemical shifts were reported relative to SiMe$_4$ (benzene-d_6: δH = 7.16 ppm and δC = 128.1 ppm, THF-d_8: δH = 1.78, 3.58 ppm and δC = 67.2, 25.3 ppm).[24] The ^{29}Si NMR chemical shifts were referenced to external SiMe$_4$. The following abbreviations were used for the multiplicities: s—singlet, d—doublet, t—triplet, sept—septet, m—multiplet, brs/brd/brt—broad singlet/doublet/triplet. IR data of powder samples were acquired on a Bruker Vertex 70 spectrometer in attenuated total reflectance mode. Melting points were determined under argon in sealed NMR tubes. The molten samples were examined by NMR spectroscopy to confirm whether decomposition had occurred upon melting.

Synthesis of Bis(germaamidine) 2 and Tetraazagermole 3 from Bis(digermene) 1: A solution of bis(digermene) **1** (1.00 g, 536 μmol, 1 eq.) in 6 mL of benzene is added dropwise to a solution of 1-adamantyl azide (1.71 g, 9.64 mmol, 18 eq.). Immediate gas formation is observed, followed by precipitation of a colorless solid overnight. Concentration to half the volume leads to further precipitation. Filtration from the mother liquor, washing four times with overall 5 mL of benzene, followed by drying in vacuum, yields bis(germaamidine) **2** (553 mg, 367 μmol, 69%). Single crystals of **2** suitable for X-ray analysis are obtained from a concentrated benzene solution. From the mother liquor of the filtration tetraazagermole **3** are obtained as a colorless crystalline solid (519 mg, 644 μmol, 60%). Single crystals of tetraazagermole **3** suitable for X-ray analysis are obtained from a concentrated pentane solution.

Although only 8 eq. of 1-AdN$_3$ are necessary for the reaction, as confirmed by multinuclear NMR spectroscopy, using an excess has been found to facilitate product separation by crystallization and to increase the isolated yields.

^{1}H NMR (400.13 MHz, THF-d$_8$, 300 K, TMS): δ = 8.61 (s, 2H, Ph*H*), 7.13 (s, 4H, Tip*H*), 3.58 (sept, 4H, C*H*(CH$_3$)$_2$ of Tip, overlapping with THF-d$_8$ peak), 2.90 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.75 (s, 12H, N(C*H*$_3$)$_2$), 1.93 (brs, 6H, C*H* of Ad), 1.83 (brs, 12H, CH(C*H*$_3$)$_2$ of Tip), 1.79–1.76 (m, 18H, C*H* and C*H*$_2$ of Ad), 1.56 (brs, 12H, CH(C*H*$_3$)$_2$ of Tip), 1.43–1.31 (m, 36H, C*H*$_2$ of Ad), 1.25 (d, 12H, CH(C*H*$_3$)$_2$ of Tip), 0.78 (s, 12H, Si(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, THF-d$_8$, 300 K, TMS): δ = 155.5, 152.3 (Ph*C*), 152.0, 146.7, 142.2, 132.3 (Tip*C*), 123.2 (Ph*C*), 58.5, 56.8 (Ad*C*N), 50.7 (N(*C*H$_3$)$_2$), 48.2, 47.6 (*C*H$_2$ of Ad), 37.3, 37.2, 36.6, 34.9 (*C*H$_2$ of Ad and *C*H(CH$_3$)$_2$ of Tip), 31.6, 31.5 (*C*H of Ad), 26.6, 24.0, 23.8 (CH(*C*H$_3$)$_2$ of Tip), 8.1 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (79.49 MHz, THF-d$_8$, 300 K, TMS): δ = −5.4 ppm. **Elemental analysis:** Calcd. for ($C_{84}H_{132}Ge_2N_6Si_2$): C, 70.68; H, 9.32; N, 5.89. Found: C, 71.95; H, 8.80; N, 6.09. **Mp.:** 202 °C (under unselective decomposition to unidentified products).

Tetraazagermole **3**:

^{1}H NMR (400.13 MHz, THF-d$_8$, 300 K, TMS): δ = 7.09 (d, 2H, Tip*H*), 7.00 (d, 2H, Tip*H*), 4.07 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.84 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.71 (sept, 2H, C*H*(CH$_3$)$_2$ of Tip), 2.11–2.01 (m, 18H, C*H* and C*H*$_2$ of Ad), 1.66–1.56 (m, 12H, C*H*$_2$ of Ad), 1.36 (d, 6H, CH(C*H*$_3$)$_2$ of Tip), 1.20 (two overlapping d, 12H, CH(C*H*$_3$)$_2$ of Tip), 1.11 (d, 6H, CH(C*H*$_3$)$_2$ of Tip), 1.03 (d, 6H, CH(C*H*$_3$)$_2$ of Tip) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, THF-d$_8$, 300 K, TMS): δ = 153.4, 153.1, 151.1, 141.9, 124.8, 122.8 (Tip*C*), 60.0 (Ad*C*N), 45.2, 37.2 (*C*H$_2$ of Ad), 36.6, 34.8, 32.9 (*C*H(CH$_3$)$_2$ of Tip), 31.2 (*C*H of Ad), 27.7, 26.2, 24.9, 24.1, 23.9, 23.9 (CH(*C*H$_3$)$_2$ of Tip) ppm. **Elemental analysis:** Calcd. for ($C_{41}H_{66}GeN_2$): C, 74.66; H, 10.09; N, 4.25. Found: C, 72.50; H, 9.25; N, 4.30. **Mp.:** 193 °C (under decomposition to 1AdN$_3$ and unidentified by-products).

Isolation of Intermediate Digermaaziridine 9: A solution of 1-adamantyl azide (198.2 mg, 1.12 mmol, 2 eq.) in 2 mL of toluene is added to a suspension of bis(digermene) **1** (1.0 g, 559 μmol, 1 eq.) in

4.2 mL of benzene at −85 °C. The resulting solution is allowed to warm to room temperature overnight. The solvent is removed under vacuum, providing a yellow foam. Single crystals of digermaaziridine **9** (29.4 mg, 25.9 μmol, 5%) are obtained from a solution in diethyl ether at 4 °C.

^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K, TMS): δ = 7.25, 7.12 (each d, each 1H, Tip*H*), 7.10 (s, 1H, Tip*H*), 7.08 (d, 1H, Tip*H*), 7.04, 7.03, 7.02 (each d, overall 4H, Tip*H*), 4.29, 4.20, 4.09, 3.80 (each sept, each 1H, *o*-*CH*(CH$_3$)$_2$ of Tip), 3.71–3.56 (m, 3H, *o*-*CH*(CH$_3$)$_2$ of Tip), 3.33 (sept, 1H, *o*-*CH*(CH$_3$)$_2$ of Tip), 2.85–2.61 (m, 4H, *p*-*CH*(CH$_3$)$_2$ of Tip), 2.18–2.15 (m, 7H, *CH* and *CH*$_2$ of Ad), 2.11–2.09 (m, 2H, *CH* and *CH*$_2$ of Ad), 1.77–1.69 (m, 5H, *CH* and *CH*$_2$ of Ad), 1.65 (brs, 1H, *CH* and *CH*$_2$ of Ad), 1.61 (d, 3H, CH(*CH*$_3$)$_2$ of Tip), 1.49 (t, 7H, CH(*CH*$_3$)$_2$ of Tip), 1.43, 1.39, 1.36 (each d, overall 7H, CH(*CH*$_3$)$_2$ of Tip), 1.28 (d, 9H, CH(*CH*$_3$)$_2$ of Tip), 1.23 (t, 9H, CH(*CH*$_3$)$_2$ of Tip), 1.16, 1.11 (each d, overall 21H, CH(*CH*$_3$)$_2$ of Tip), 0.99 (d, 3H, CH(*CH*$_3$)$_2$ of Tip), 0.81 (d, 3H, CH(*CH*$_3$)$_2$ of Tip), 0.75 (d, 3H, CH(*CH*$_3$)$_2$ of Tip), 0.59, 0.57 (each d, overall 7H, CH(*CH*$_3$)$_2$ of Tip) ppm.

Reaction of Tip$_2$Ge=GeTip$_2$ with 1-Adamantyl Azide: A solution of 1-adamantyl azide (22.2 mg, 125 μmol, 4 eq.) in 0.2 mL of C$_6$D$_6$ is added to a solution of the digermene (30 mg, 31.3 μmol, 1 eq.) in 0.3 mL of C$_6$D$_6$. The resulting yellow solution is heated at 65 °C for 11 hr. ^{1}H NMR spectroscopy confirmed the integrity of Tip$_2$Ge=GeTip$_2$.

Reaction of Bis(digermene) 1 with Hexanol: To a solution of bis(digermene) **1** (50.0 mg, 26.2 μmol, 1 eq.) in 0.5 mL of C$_6$D$_6$ in an NMR tube, hexanol (6.6 μL, 52.4 μmol, 2 eq.) is added. Full conversion to the bis(siloxane) is confirmed by multinuclear NMR spectroscopy.

^{1}H NMR (300.13 MHz, C$_6$D$_6$, 300 K, TMS): δ = 7.92 (s, 2H, Me$_2$N-Ph*H*), 3.78 (t, 4H, O*CH*$_2$(CH$_2$)$_4$CH$_3$), 2.56 (s, 12H, N(*CH*$_3$)$_2$), 1.83–1.67 (m, 4H, OCH$_2$*CH*$_2$(CH$_2$)$_3$CH$_3$ overlapping with peaks of unidentified by-products), 1.55–1.23 (m, 12H, O(CH$_2$)$_2$(*CH*$_2$)$_3$CH$_3$ overlapping with peaks of unidentified by-products), 1.21–1.17 (m, 4H, O(CH$_2$)$_5$*CH*$_3$ overlapping with peaks of unidentified by-products), 0.95–0.83 (m, 6H, O(CH$_2$)$_5$*CH*$_3$ overlapping with signals of decomposition products of Tip$_2$Ge=GeHTip), 0.54 (s, 12H, Si(*CH*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (75.47 MHz, C$_6$D$_6$, 300 K, TMS): δ = 158.0, 139.9 (Ph*C*$_{\text{quart}}$), 129.3 (Ph*C*), 63.1 (O*C*H$_2$(CH$_2$)$_4$CH$_3$), 47.0 (N(*C*H$_3$)$_2$), 34.8, 34.7 (OCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_3$), 26.3, 26.1 (O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 24.2, 24.1 (O(CH$_2$)$_3$CH$_2$*C*H$_2$CH$_3$), 23.2, 23.1 (O(CH$_2$)$_4$*C*H$_2$CH$_3$), 14.4, 14.3 (O(CH$_2$)$_5$*C*H$_3$), −0.3 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (59.63 MHz, C$_6$D$_6$, 300 K, TMS): δ = 3.5 ppm.

Synthesis of Bis(germaamidine) 2 from NHC-Bis(germylene) 10: A solution of 1-adamantyl azide (461 mg, 2.60 mmol, 4 eq.) in 25 mL of benzene is added to a suspension of NHC-bis(germylene) **10** (800 mg, 650 μmol, 1 eq.) in 30 mL of benzene, resulting in gas formation and a rapid color change from yellow to red to pale yellow. After stirring at ambient temperature for 17 hr, the solvent is removed and the residue is washed three times with overall 3 mL of pentane and dried under vacuum. Bis(germaamidine) **2** is obtained as a colorless solid in 40% yield (386.9 mg, 263 μmol)*.

* 3wt% NHC impurity contained.

Synthesis of Bis(germaamidine) 2 from CAAC-Bis(germene) 11: Bis(germene) **11** (300 mg, 214 μmol, 1 eq.) and 1-adamantyl azide (226.9 mg, 1.28 mmol, 6 eq.) are suspended in 17 mL of benzene and heated to 65 °C. After heating to 65 °C for 24 hr, the solvent is removed under vacuum and the residue is washed twice with overall 3 mL of a mixture of pentane and benzene (2:1). The resulting colorless solid is dried in vacuum to yield 68% of bis(germaamidine) **2** (237 mg, 146 μmol)*. ^{1}H NMR spectroscopy of the reaction mixture confirmed the formation of CAAC-N$_3$Ad in a 2:1 ratio with bis(germaamidine) **2**.

* 12wt% of CAAC=N$_3$Ad impurity contained.

Synthesis of CAAC=N$_3$Ad 12: The CAAC 1-(2,6-diisopropylphenyl)−3,3,5,5-tetramethyl-pyrrolidin-2-ylidene (100 mg, 351 μmol, 1 eq.) and 1-adamantyl azide (62.1 mg, 351 μmol, 1 eq.) are dissolved in 2.5 mL of benzene at ambient temperature for one hour. The solvent is removed under vacuum and dissolved in a mixture of 2 mL of pentane and 1 mL of benzene. Storing at 4 °C yields single crystals of **12**. Removing the solvent of the mother liquor under vacuum provides **12** as colorless amorphous powder in an overall yield of 84% (136.1 mg, 294 μmol).

^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K, TMS): δ = 7.24 (dd, 1H, DipH), 7.13, 7.12 (overlapping d, 2H, DipH), 3.12 (sept, 2H, *CH*(CH$_3$)$_2$ of Dip), 2.02 (m, 3H, *CH* of Ad), 1.99 (d, 6H, *CH*$_2$ of Ad), 1.80 (s, 2H, *CH*$_2$ of CAAC), 1.69 (s, 6H, *CH*$_3$ of CAAC), 1.61 (t, 6H, *CH*$_2$ of Ad), 1.29 (d, 6H, CH(*CH*$_3$)$_2$ of Dip), 1.24 (d, 6H, CH(*CH*$_3$)$_2$ of Dip), 1.04 (s, 6H, *CH*$_3$ of CAAC) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, C$_6$D$_6$, 300 K, TMS): δ = 178.0 (CAAC-*C*), 148.4, 132.4, 128.8, 124.2 (Dip*C*), 63.8, 63.2 (CAAC-*C*(CH$_3$)$_2$), 54.5 (*C*H$_2$ of CAAC), 42.7, 42.2 (Ad*C*N and *C*H$_2$ of Ad), 37.1, 29.9, 29.7 (*C*H and *C*H$_2$ of Ad and *C*H(CH$_3$)$_2$ of Dip), 29.2, 26.3, 22.9 (CAAC-C(*C*H$_3$)$_2$ and CH(*C*H$_3$)$_2$ of Dip) ppm. **Elemental analysis:** Calcd. for (C$_{30}$H$_{46}$N$_4$): C, 77.87; H, 10.02; N, 12.11. Found: C, 76.88; H, 8.84; N, 11.86. **Mp.:** 188 °C (under partial decomposition, presumably to the CAAC = NAd).

After melting, partial decomposition to a product, which could be the CAAC = NAd imine according to the NMR data:

^{1}H NMR (400.13 MHz, 300 K, TMS): δ (C$_6$D$_6$) = 7.20 (d, 2H, DipH), 7.18 (d, 1H, DipH), 3.26 (sept, 2H, *CH*(CH$_3$)$_2$ of Dip), 1.91 (d, 5H, *CH*$_2$ of Ad), 1.85 (m, 2H, *CH*$_2$ of CAAC), 1.74 (t, 7H, *CH*$_2$ of of Ad), 1.52 (brs, 3H, *CH* of Ad), 1.40 (s, 6H, *CH*$_3$ of CAAC), 1.38, 1.33, 1.31 (each s, overall 6H, CH(*CH*$_3$)$_2$ of Dip), 1.07 (s, 6H, CH(*CH*$_3$)$_2$ of Dip), 1.02 (brs, 6H, *CH*$_3$ of CAAC) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, C$_6$D$_6$, 300 K, TMS): δ = 160.7 (CAAC-*C*), 149.8, 135.3, 123.7 (Dip*C*), 57.9, 57.0 (CAAC-*C*(CH$_3$)$_2$), 53.1 (*C*H$_2$ of CAAC), 46.4, 40.3 (Ad*C*N and *C*H$_2$ of Ad), 38.0, 30.7, 30.1 (*C*H and *C*H$_2$ of Ad and *C*H(CH$_3$)$_2$ of Dip), 29.0, 28.7, 27.2, 23.4 (CAAC-C(*C*H$_3$)$_2$ and CH(*C*H$_3$)$_2$ of Dip) ppm.

Reaction of Bis(germaamidine) 2 with Carbon Dioxide: Bis(germaamidine) **2** (100 mg, 66.4 μmol) is dissolved in 4 mL of benzene. The resulting solution is stirred under a CO$_2$ atmosphere at ambient pressure for three hours. Single crystals are grown from this solution to yield bis(germaoxazetidinone) **13** (40.5 mg, 26.7 μmol, 40%).

^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K, TMS): δ = 8.43 (s, 2H, Ph*H*), 7.16 (s, 4H, Tip*H*), 4.18, 4.00 (overlapping brs, 4H, *o*-*CH*(CH$_3$)$_2$ of Tip), 2.88 (s, 12H, N(*CH*$_3$)$_2$), 2.67 (sept, 2H, *p*-*CH*(CH$_3$)$_2$ of Tip), 2.33, 2.27 (overlapping brt, 22H, *CH* and *CH*$_2$ of Ad), 1.94, 1.89 (brd, 12H, *CH* and *CH*$_2$ of Ad), 1.55–1.36 (m, 26H, *CH* and *CH*$_2$ of Ad), 1.51 (d, 24H, *o*-CH(*CH*$_3$)$_2$ of Tip, overlapping with signals of *CH* and *CH*$_2$ of Ad), 1.11, 1.11 (each d, 12H, *p*-CH(*CH*$_3$)$_2$ of Tip), 0.89 (s, 6H, Si(*CH*$_3$)$_2$), 0.51 (brs, 6H, Si(*CH*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, THF-d$_8$, 300 K, TMS): δ = 157.6 (*C*=O), 156.6 (Ph*C*), 152.7, 140.6, 135.4, 132.0 (Tip*C*), 128.6 (Ph*C*), 59.6, 55.0 (Ad*C*N), 47.5 (brs, *C*H$_2$ of Ad), 46.2 (N(*C*H$_3$)$_2$), 42.9 (*C*H$_2$ of Ad), 36.7, 36.3, 34.5 (*C*H$_2$ of Ad and *C*H(CH$_3$)$_2$ of Tip), 31.1, 30.2 (*C*H of Ad), 26.7, 24.4, 23.9, 23.9 (CH(*C*H$_3$)$_2$ of Tip), 8.0, 6.6 (Si(*C*H$_3$)$_2$) ppm. **^{29}Si{^{1}H} NMR** (79.49 MHz, C$_6$D$_6$, 300 K, TMS): δ = −5.2 ppm. **Elemental analysis:** Calcd. for (C$_{89}$H$_{135}$Ge$_2$N$_6$O$_4$Si$_2$): C, 68.77; H, 8.75; N, 5.41. Found: C, 68.24; H, 7.57; N, 5.48. **Mp.:** 274 °C (under unselective decomposition to a mixture of unidentified products). **IR:** ν(CO) 1720 cm^{-1}.

Reaction of Bis(germaamidine) 2 with Methanol: A solution of methanol in THF (1.56 M, 0.2 ML, 256 μmol, 2.8 eq.) is added dropwise to a suspension of bis(digermene) **1** (156.2 mg, 110 μmol, 1 eq.) in 10 mL of benzene. After stirring at ambient temperature for two hours, the solvent is removed under vacuum. The crude product is dissolved in 1 mL of pentane and filtered via canula. Removing the solvent of the mother liquor yields the hydroalkoxylation product **14** as a colorless powder (52.5 mg, 35.2 μmol, 32%). Single crystals suitable for X-ray crystallography are obtained from a benzene solution.

^{1}H NMR (400.13 MHz, C_6D_6/THF-d_8, 300 K, TMS): $\delta = 7.94$ (s, 2H, Ph*H*), 7.14 (s, 4H, Tip*H*), 4.55, 4.24 (overlapping brs, 4H, *o*-C*H*$(CH_3)_2$ of Tip), 3.88 (d, 6H, N$(CH_3)_2$), 3.51 (s, 6H, OMe, overlapping with THF-d_8 peaks), 2.74 (sept, 2H, *p*-C*H*$(CH_3)_2$ of Tip), 2.67 (s, 12H, N$(CH_3)_2$), 2.25 (s, 12H, *CH* of Ad), 1.83 (s, 12H, CH_2 of Ad), 1.70–1.61 (m, 12H, CH_2 of Ad, overlapping with NH peaks), 1.60 (brs, 2H, NH, overlapping with peaks from Ad), 1.52–1.43 (m, 36H, CH_2 of Ad and *o*-CH$(CH_3)_2$ of Tip, overlapping with THF-d_8 peak), 1.35 (s, 12H, CH_2 of Ad), 1.15 (d, 12H, *p*-CH$(CH_3)_2$ of Tip), 0.92, 0.82 (each s, each 6H, Si$(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (100.61 MHz, C_6D_6/THF-d_8, 300 K, TMS): $\delta = 156.1$ (Ph*C*), 153.5, 150.3, 144.3, 140.2, 131.6 (Tip*C*), 128.59 (Ph*C*), 58.5, 52.8 (Ad*C*N), 51.5, 51.5 (OMe), 47.6 (CH_2 of Ad), 47.2 (N$(CH_3)_2$), 46.6 (CH_2 of Ad), 41.6 (brs, CH_2 of Ad), 36.8, 36.5, 36.0, 34.4 (CH_2 of Ad and *C*H$(CH_3)_2$ of Tip), 31.4, 30.8 (*C*H of Ad), 25.9, 25.6, 24.0, 24.0 (CH$(CH_3)_2$ of Tip), 9.7, 9.2 (Si$(CH_3)_2$) ppm. **^{29}Si{^{1}H} NMR** (79.49 MHz, C_6D_6/THF-d_8, 300 K, TMS): $\delta = -7.05, -7.09$ ppm. **Elemental analysis:** Calcd. for ($C_{92}H_{146}Ge_2N_6O_2Si_2$): C, 70.40; H, 9.38; N, 5.35. Found: C, 71.58; H, 7.78; N, 7.04. **Mp.:** 126 °C (under partial decomposition).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] a) F. Doraghi, S. Karimian, H. Navid, M. Ghanbarlou, B. Larijani, M. Mahdavi, *Monatsh. Chem.* **2024**, *155*, 419; b) Y. Zuo, P. Zuo, M. Liu, X. Wang, J. Du, X. Li, P. Zhang, Z. Xu, *Org. Biomol. Chem.* **2024**, *22*, 5014; c) W. Guo, M. Zhao, W. Tan, L. Zheng, K. Tao, X. Fan, *Org. Chem. Front.* **2019**, *6*, 2120; d) A. A. Aly, S. Bräse, M. A. M. Gomaa, *ARKIVOC.* **2018**, *2018*, 85; e) T. Ishikawa, T. Kumamoto, in *Superbases for Organic Synthesis* John Wiley & Sons, UK **2009**, pp. 49–91.

[2] a) J. S. Fisherman, E. M. Cline, J. Plowman, F. R. Quinn, M. J. Hawkins, *Invest. New Drugs* **1991**, *9*, 295; b) N. Yang, L. Yang, X. Zhu, P. Zhao, H. Liu, C. Xia, S. Dai, C. Tian, *ACS Mater. Lett.* **2022**, *4*, 2143; c) Y. Zheng, N. A. Khan, X. Ni, K. A. I. Zhang, Y. Shen, N. Huang, X. Y. Kong, L. Ye, *Chem. Commun.* **2023**, *59*, 6314; d) O. Buyukcakir, J. Ryu, S. H. Joo, J. Kang, R. Yuksel, J. Lee, Y. Jiang, S. Choi, S. H. Lee, S. K. Kwak, S. Park, R. S. Ruoff, *Adv. Funct. Mater.* **2020**, *30*, 2003761; e) L. Geng, J. Wang, X. Yang, J. Jiang, R. Li, Y. Yan, J. Zhao, C. Liu, *Chem. Eng. J.* **2024**, *487*, 150749.

[3] a) P. P. Power, *J. Chem. Soc., Dalton Trans.* **1998**, 2939; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463; c) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877; d) D. Scheschkewitz, *Chem. Lett.* **2011**, *40*, 2; e) A. Rammo, D. Scheschkewitz, *Chem. Eur. J.* **2018**, *24*, 6866; f) T. Matsuo, N. Hayakawa, *Sci. Technol. Adv. Mater.* **2018**, *19*, 108; g) A. Agarwal, S. K. Bose, *Chem. Asian J.* **2020**, *15*, 3784; h) C. Weetman, *Chem. Eur. J.* **2021**, *27*, 1941; i) S. Fujimori, Y. Mizuhata, N. Tokitoh, *Proc. Jpn. Acad., Ser. B* **2023**, *99*, 480; j) V. Y. Lee, *Molecules* **2023**, *28*, 1558; k) M. Karni, Y. Apeloig, in *Organogermanium Compounds*, (Ed.: V. Y. Lee), John Wiley & Sons, Hoboken, NJ, USA **2023**, pp. 1–102; l) V. Y. Lee, in *Organogermanium Compounds*, (Ed.: V. Y. Lee), John Wiley & Sons, Hoboken, NJ, USA **2023**, pp. 435–475; m) K. V. Zaitsev, in *Organogermanium Compounds*, (Ed.: V. Y. Lee), John Wiley & Sons, Hoboken, NJ, USA **2023**, pp. 103–193; n) C. Duan, C. Cui, *Chem. Soc. Rev.* **2024**, *53*, 361; o) A. Fukazawa, Y. Li, S. Yamaguchi, H. Tsuji, K. Tamao, *J. Am. Chem. Soc.* **2007**, *129*, 14164; p) K. Tamao, M. Kobayashi, T. Matsuo, S. Furukawa, H. Tsuji, *Chem. Commun.* **2012**, *48*, 1030; q) L. Li, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *J. Am. Chem. Soc.* **2015**, *137*, 15026; r) L. Klemmer, A.-L. Thömmes, M. Zimmer, V. Huch, B. Morgenstern, D. Scheschkewitz, *Nat. Chem.* **2021**, *13*, 373; s) A.-L. Thömmes, T. Büttner, B. Morgenstern, O. Janka, G. Kickelbick, B.-J. Niebuur, T. Kraus, M. Gallei, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2024**, *63*, e202415103.

[4] T. Ohtaki, Y. Kabe, W. Ando, *Heteroat. Chem* **1994**, *5*, 313.

[5] a) N. Wiberg, K. Schurz, G. Reber, G. Müller, *J. Chem. Soc., Chem. Commun.* **1986**, 591; b) J. Niesmann, U. Klingebiel, M. Schäfer, R. Boese, *Organometallics* **1998**, *17*, 947; c) T. Iwamoto, N. Ohnishi, Z. Gui, S. Ishida, H. Isobe, S. Maeda, K. Ohno, M. Kira, *New J. Chem.* **2010**, *34*, 1637.

[6] a) M. Denk, R. K. Hayashi, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 10813; b) D. Liu, D. Zhou, H. Yang, J. Li, C. Cui, *Chem. Commun.* **2019**, *55*, 12324; c) P. Hädinger, M. P. Müller, A. Hinz, *Inorg. Chem.* **2024**, *63*, 1997; d) D. Jin, X. Sun, A. Hinz, P. W. Roesky, *Inorg. Chem.* **2024**, *63*, 18669.

[7] a) W. Ando, T. Ohtaki, Y. Kabe, *Organometallics* **1994**, *13*, 434; b) J. Schneider, K. M. Krebs, S. Freitag, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2016**, *22*, 9812; c) T. Li, L. Zhang, Y. He, Y. Chen, D. Wang, J. Liu, G. Tan, *Chem. Commun.* **2023**, *59*, 1533.

[8] a) G. Ossig, A. Meller, S. Freitag, R. Herbst-Irmer, *J. Chem. Soc., Chem. Commun.* **1993**, 497; b) M. J. Evans, J. M. Parr, D. T. Nguyen, C. Jones, *Chem. Commun.* **2024**, *60*, 10350; c) A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1991**, 1123; d) H. Schäfer, W. Saak, M. Weidenbruch, *Z. Kristallogr. NCS.* **2000**, *215*, 453; e) M. J. Evans, M. D. Anker, A. Mouchfiq, M. Lein, J. R. Fulton, *Chem. Eur. J.* **2020**, *26*, 2606; f) M. J. Evans, F. M. Burke, P. M. Chapple, J. R. Fulton, *Inorg. Chem.* **2021**, *60*, 8293; g) R. Guthardt, L. Oetzel, T. Lang, C. Bruhn, U. Siemeling, *Chem. Eur. J.* **2022**, *28*, e202200996.

[9] M. Fischer, M. M. D. Roy, L. L. Wales, M. A. Ellwanger, C. McManus, A. F. Roper, A. Heilmann, S. Aldridge, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211616.

[10] M. Veith, S. Becker, V. Huch, *Angew. Chem. Int. Ed., Engl.* **1990**, *29*, 216.

[11] V. S. Ajithkumar, P. B. Ghanwat, K. V. Raj, K. Vanka, R. G. Gonnade, S. S. Sen, *Organometallics* **2023**, *42*, 2983.

[12] a) W. Ando, T. Tsumuraya, *Organometallics* **1988**, *7*, 1882; b) S. A. Batcheller, S. Masamune, *Tetrahedron Lett.* **1988**, *29*, 3383; c) T. Tsumuraya, S. Sato, W. Ando, *Organometallics* **1990**, *9*, 2061.

[13] A.-L. Thömmes, B. Morgenstern, M. Zimmer, D. M. Andrada, D. Scheschkewitz, *Chem. Eur. J.* **2023**, *29*, e202301273.

[14] A. I. Ojeda-Amador, J. Munarriz, P. Alamán-Valtierra, V. Polo, R. Puerta-Oteo, M. V. Jiménez, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, *ChemCatChem* **2019**, *11*, 5524.

[15] A.-L. Thömmes, R. Völker, B. Morgenstern, M. Zimmer, D. Munz, C. W. M. Kay, D. Scheschkewitz, *Inorg. Chem. Front.* **2025**, *12*, 4835.

[16] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans.* **1987**, *2*, 1.

[17] a) H. Preut, R. C. Obloh, W. P. Neumann, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1988**, *44*, 574; b) J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.* **1989**, *122*, 245; c) M. Veith, E. Werle, V. Huch, *Z. Anorg. Allg. Chem.* **1993**, *619*, 641.

[18] H. Schäfer, W. Saak, M. Weidenbruch, *Organometallics* **1999**, *18*, 3159.

[19] N. Kuhn, T. Kratz, *Synthesis* **1993**, *1993*, 561.

[20] D. Dhara, L. Endres, I. Krummenacher, M. Arrowsmith, R. D. Dewhurst, B. Engels, R. Bertermann, M. Finze, S. Demeshko, F. Meyer, F. Fantuzzi, H. Braunschweig, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401052.

[21] a) H. Imoto, K. Naka, *Polymer* **2022**, *241*, 124464; b) C. S. Weinert, in *Organogermanium Compounds*, (Ed.: V. Y. Lee), John Wiley & Sons, Hoboken, NJ, USA **2023**, pp. 787–837; c) M. Gon, K. Tanaka, *Smart Mol.* **2025**, e20240064; d) S. Ito, K. Tanaka, *Polym. Chem.* **2025**, *16*, 2046.

[22] F. Vollmer, W. Rettig, E. Birckner, *J. Fluoresc.* **1994**, *4*, 65.

[23] a) C. Müller, D. M. Andrada, I.-A. Bischoff, M. Zimmer, V. Huch, N. Steinbrück, A. Schäfer, *Organometallics* **2019**, *38*, 1052; b) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705; c) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851; d) C. M. Weinstein, G. P. Junor, D. R. Tolentino, R. Jazzar, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2018**, *140*, 9255.

[24] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

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